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# Toward the synthesis of catalytic conducting metallopolymer for cross-coupling reactions

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# Toward the synthesis of a catalytic conducting metallopolymer for cross-coupling reactions

**by**

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**Thesis**

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# Dedication

To my parents,

Thank you for all the support and encouragement.

# Acknowledgements

I want to thank Dr. Jones for all the help for this work, especially since Dr. Holliday left.

I want to thank Dr. Holliday for the idea and help for this work.

I want to thank Claudina, Dan and Leander for the proofread of this work.

# Abstract

## Toward the synthesis of catalytic a conducting metallopolymer for cross-coupling reactions

**Weiran Wang, M.A.**

The University of Texas at Austin, 2016

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The thiophene-based metallopolymer provides a great template for redox-active catalysts. Chemical or electrochemical doping of the metallopolymer can generate charged species within the polymer backbone thereby tuning the electronic nature of the bound metals. The metal-ligand bond strength and the catalytic activity in such a conducting metallopolymer can be tuned directly by applying different potential to the material. Thiophene-functionalized *N*-heterocyclic carbene (NHC) based palladium complexes are believed to be catalytically active for cross-coupling reactions and electropolymerizable into the metallopolymer. The tenability of the resulting metallopolymers as cross-coupling reaction catalysts can be evaluated by their catalytic performances under different applied voltages.

Two thiophene-functionalized benzimidazolium chloride molecules (DThBMesHCl and DThBAdHCl) were synthesized as precursors for NHC ligands. Their metalation with Pd and Ag precursors failed to generate desired metal complexes. The results were analyzed by comparison with the literature examples and the Ag metalation of

non-thiophene version of the benzimidazolium chloride molecule. The major obstacles for the metalation were concluded to be the steric hindrance from the bulky *N*-substituent and/or the lack of acidity of the imidazolium moiety.

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# 1. Introduction

## 1.1 Redox-active ligands

Redox-active ligands provide a great option for a ligand-based approach in tuning the reactivity of metal complexes. Redox-active ligands incorporate redox-active groups into the structure and can influence the reactivity of the metal center as a function of structural and/or electronic density change of the ligand under different oxidation states. Allgeier and Mirkin[1] classified the redox-active ligands into three categories (Figure 1).

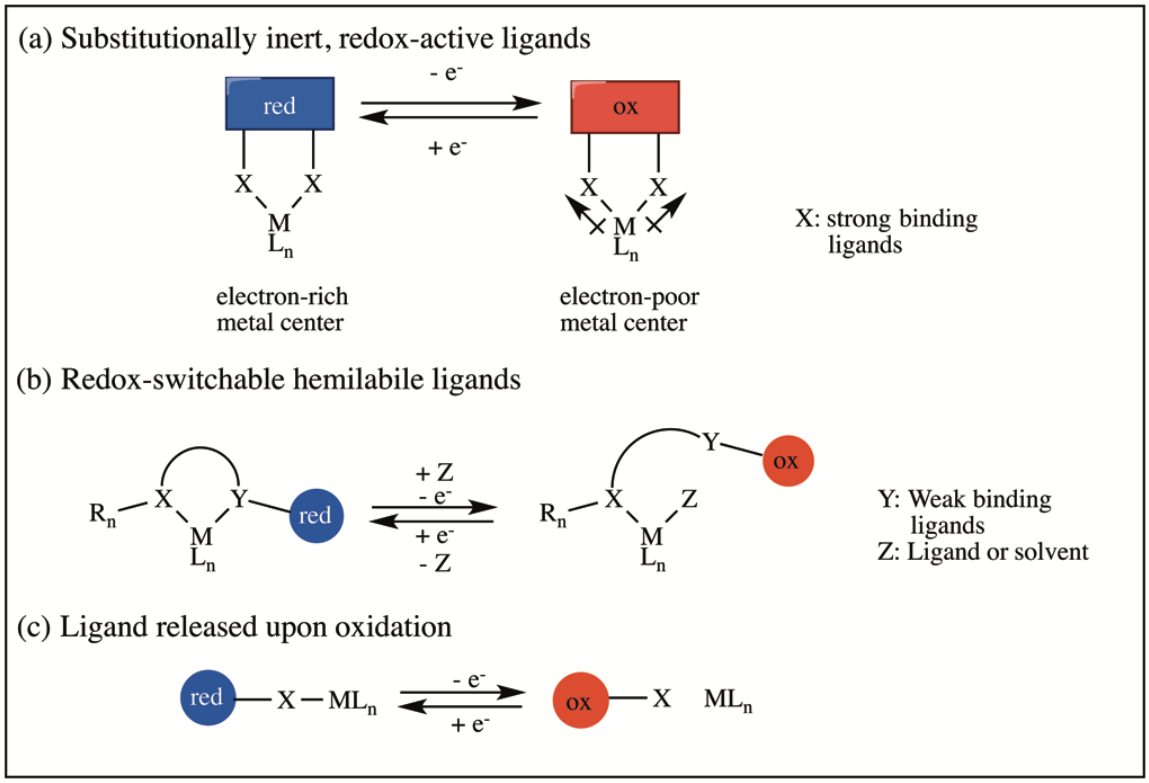



**Figure 1.** Classification of redox-active ligands.

Substitutionally inert redox active (SIRA) ligands incorporate the redox-active group into strongly binding ligands (Figure 1(a)). Altering the oxidation state of the ligand

influences the electronic nature of the bound metal without changing the chemical structure of the complex. Redox-switchable hemilabile ligands consist of one or more strongly binding centers and one weakly binding center. A redox-active group is covalently attached to the weakly binding center (Figure 1(b)). Upon oxidation of the redox-active group, the strength of the metal-ligand bond decreases and in some cases results in the dissociation of the weakly binding center. Another category of the redox-active ligands are ligands that are released from the metal center upon oxidation (Figure 1(c)).

Using SIRA ligands incorporating a metallocene or quinone as the redox-active group, the reactivity of the metal complexes can be tuned by changing the oxidation state of the ligand without altering the oxidation state of the bound metal (Figure 2). Wrighton and coworkers synthesized cobaltocene-containing bis-phosphine ligands that catalyzed the reduction of cyclohexene with $H_2$ and the hydrosilylation of acetone (Figure 2(a)).[2] The complex with a reduced cobaltocene catalyzed the $H_2$ reduction reaction 15 times faster than the hydrosilylation reaction, in contrast to the complex with an oxidized cobaltocene which catalyzed the hydrosilylation reaction 15 times faster than the $H_2$ reduction. Gregson *et al*. incorporated ferrocene groups into a Ti-salen complex and its catalytic activity was controlled through oxidation/reduction of the ferrocene moieties (Figure 2(b)).[3] Oxidizing the ferrocene groups decreased the kinetic rate toward ring-opening polymerization of lactide by 30-fold. Using the same strategy, Diaconescu and coworkers designed ferrocene-containing complexes with Zr and Ti (Figure 2(c)).[4] The oxidation/reduction of the ferrocene moiety within the complex altered its selectivity over two different monomers. Reduced complex selectively polymerized L-lactide while the oxidized complex selectively polymerized ε-caprolactone. By altering the oxidation state of the ferrocene moiety, a block copolymer of L-lactide and ε-caprolactone with a narrow molecular weight distribution was synthesized through a one-pot strategy and only one catalyst.

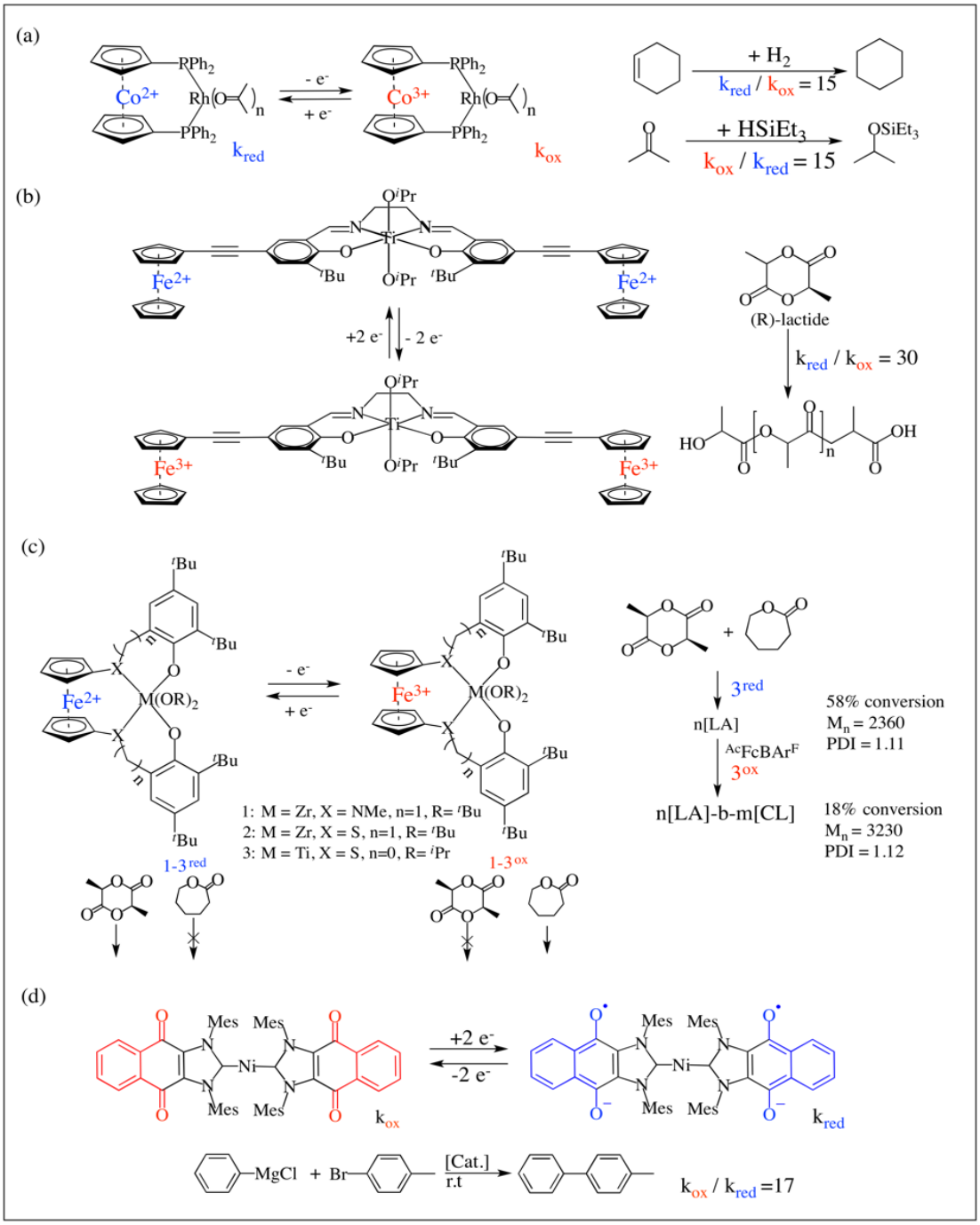



**Figure 2.** Examples of SIRA ligands for controlling reactivity of the metal complexes: (a) Cobaltocene incorporated bis-phosphine ligand.[2] (b) Ferrocene incorporated Ti-salen complexes.[3] (c) Ferrocene incorporated Ti/Zr complexes that selectively polymerize both L-lactide and ε-caprolactone.[4] (d) Naphthalene-1,4-dione incorporated NHC ligand.[5]

Organic redox-active groups also control the reactivity by electron doping onto the π-conjugation system. Naphthalene-1,4-dione was embedded into a *N*-heterocyclic carbene (NHC) based Ni complex (Figure 2(d)).[5] The reduction isomerized the di-quinone into the di-phenol with a radical and an anion on each oxygen atom. This reduced complex decreased the catalytic activity of the Kumada coupling reaction by 17-fold.

### 1.2 REDOX-ACTIVE LIGANDS WITH A π-CONJUGATED BACKBONE

π-Conjugated polymers and oligomers have been widely studied and used in many fields over the past few decades for their intrinsic electronic properties, due to their highly delocalized π-conjugated system over several repeating units. The electrical conductivity of these types of materials increases to a high level when doped chemically or electrochemically, *e.g.* doping the insulating polyacetylene (intrinsic conductivity < $10^{-5}$ $(\Omega \bullet cm)^{-1}$) with reductant or oxidant generates highly conductive materials (200 to 1000 $(\Omega \bullet cm)^{-1}$).[6] The dopant generates charged species (soliciton, polaron or bipolaron) within a limited range on the polymer backbone, which leads to the geometric deformation. This generates two new states from the LUMO (conduction band, CB) and the HOMO (valence band, VB) which results in a lower band gap. The charged species further move within the polymer backbone and transfer energy, thereby changing the electronic nature of the material. Among the π-conjugated polymeric materials, polythiophene is special. It shows metallic charge transport properties under high dopant concentration or electrochemical doping conditions. Polythiophene has a small intrinsic bandgap (~2.0 eV) when compared to other π-conjugated polymers, *e.g.* polypyrrole (~3.2 eV) or polyparaphenylene (~3.5 eV). Under high dopant concentrations or electrochemical doping conditions, both higher

and lower bipolaron states generated from the LUMO and HOMO, respectively, broaden and emerge with each other.[7]

Metal-containing hybrid materials have also been widely studied over the past 2 decades. Wolf classified the metal-containing thiophene-based hybrid materials into 3 categories (Figure 3).[8] In Wolf type 1 metallopolymers, the metal center is tethered to a π-conjugated backbone with a non-conjugated linker such as an alkyl chain. Ideally, the properties of the metal are not influenced by π-conjugated backbones in this type of metallopolymer. In Wolf type 2 metallopolymers, the metal center and the π-conjugated backbone are linked through π bonds. Coupled with the backbone, the electronic properties of the metals can be influenced by changing the electronic nature of the π-conjugated backbone. For Wolf type 3 metallopolymers, the metal center is directly embedded into the π-conjugated backbone through strong dative bonds or covalent bonds. The electrochemical properties of the metal center in this type of metallopolymer are heavily influenced by the organic moieties.

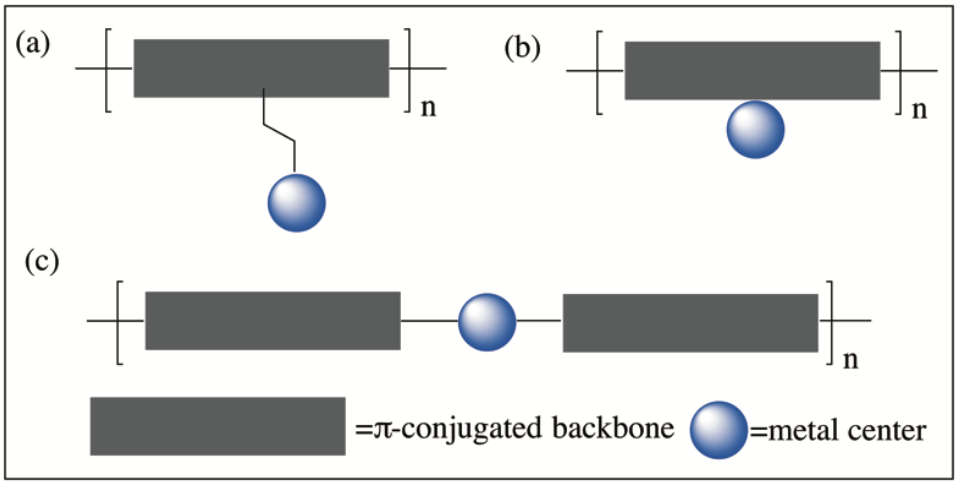



**Figure 3.** Classification of transition-metal-polythiophene metallopolymers by Wolf: (a) type 1; (b) type 2; (c) type 3.[8]

Wolf type 2 thiophene based conducting metallopolymers can be ideal templates for SIRA ligands (Figure 4). Wolf and Wrighton electropolymerized 5,5'-(2-thienyl)-2,2'-bithiazo into a thin film and further metalated this material with [Re $(CO)_3(CH_3CN)]^+$ (Figure 4(a)).[9] The conductivity of the generated metallopolymer thin film rose when the applied voltage was higher than +1.2 V. The carbonyl stretching bands under applied voltages were measured for this metallopolymer. When a voltage of +1.5 V was applied, the carbonyl stretching frequency shifted from 1934 $cm^{-1}$ to 1940 $cm^{-1}$ and from 2040 to 2044 $cm^{-1}$ respectively. However, the films showed observable degradation under applied voltages. Milum *et. al.* further demonstrated that the electron density of the metal center could be attenuated directly by applying different voltages onto the bulk material (Figure 4(b)).[10] A bithiophene-functionalized Pt-N^C^N pincer complex based conducting metallopolymer was synthesized and the vibrational frequency of Pt-CN stretching shifted from 2177 $cm^{-1}$ to 2168 $cm^{-1}$ when a voltage of +1.27 V was applied to the conductive polymer backbone. This feature further allows tuning of the reactivity of the metal center by changing the applied voltage. Raiford *et al.* functionalized a Rh-N^C^N pincer complex with bithiophene moieties and electropolymerized the complex into a metallopolymer.[11] The kinetic rate of reduction of cyclohexanone with $H_2$ by this metallopolymer thin film decreased by 60% (from 1.28 $h^{-1}$ to 0.51 $h^{-1}$) when +1.00 V was applied to the material (Figure 4(c)).[11]

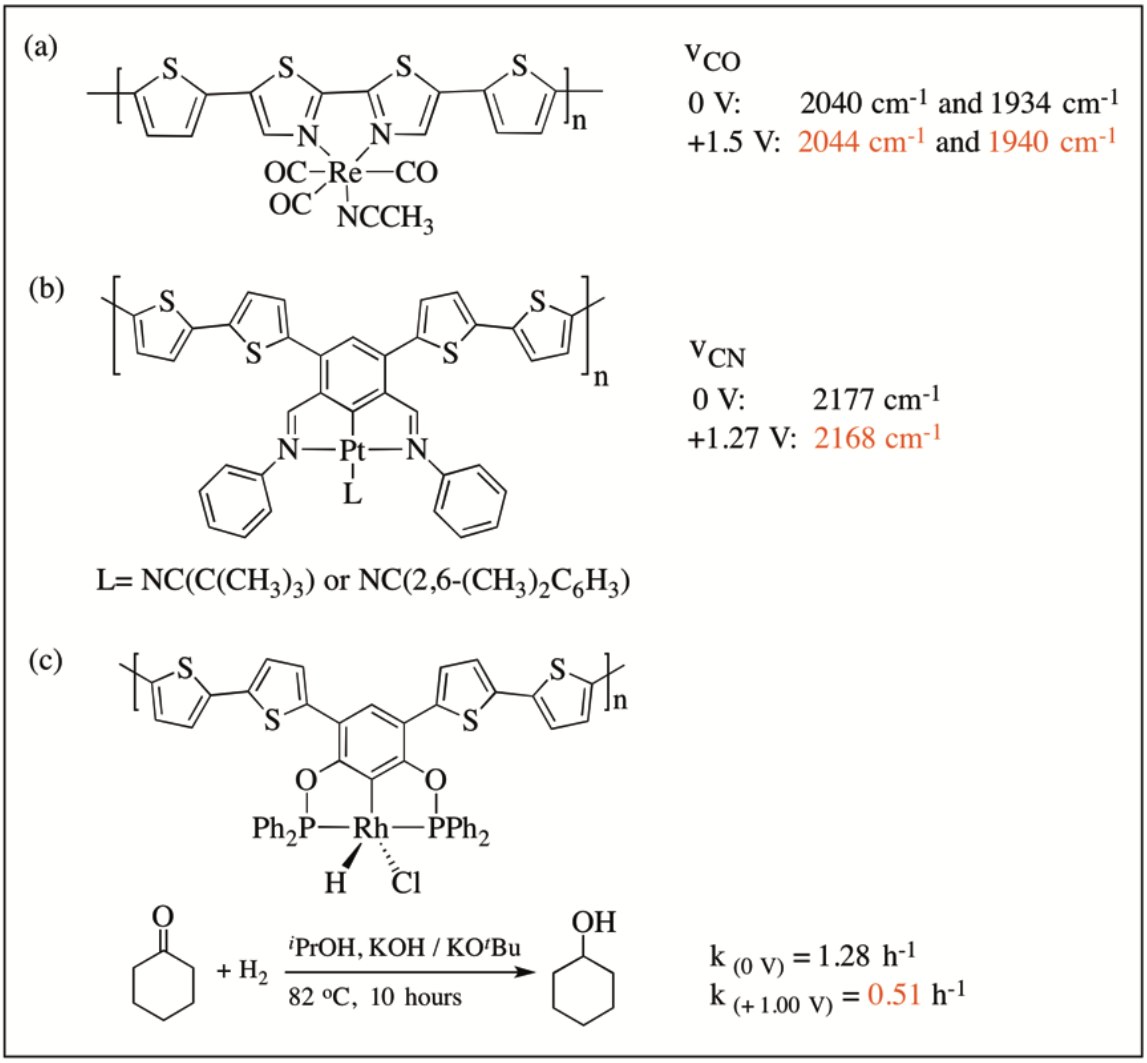


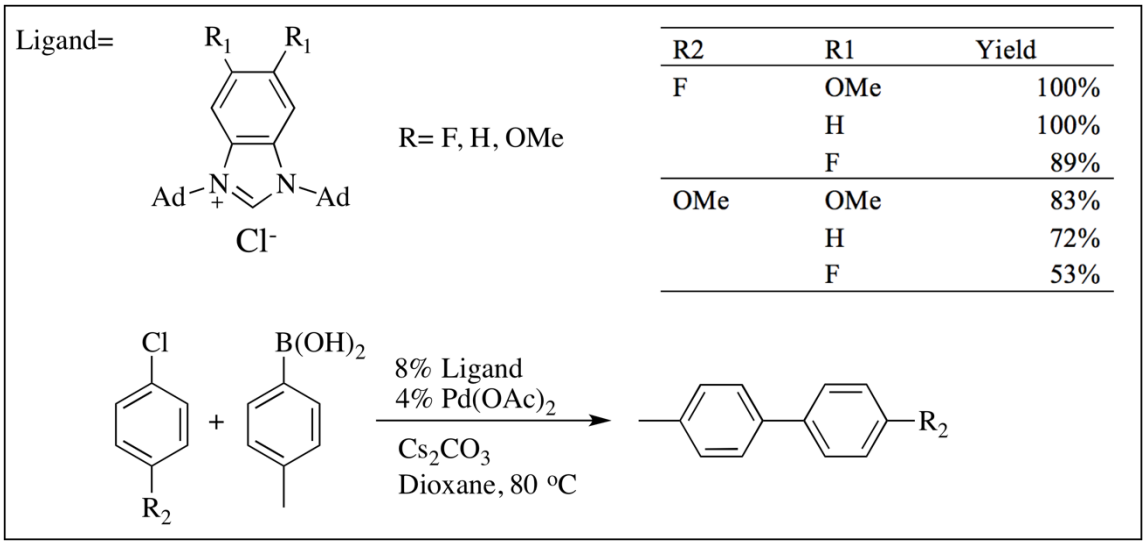

**Figure 4.** Examples of Wolf type 2 thiophene-based metallopolymers for tuning the electronic density and reactivity of the metal center: (a) Re based 5,5'-(2-thienyl)-2,2'-bithiazo metallopolymer.[9] (b) Pt-N^C^N pincer complex based metallopolymer.[10] (c) Rh-P^C^P-pincer complex based metallopolymer.[11]

## 1.3 *N*-HETEROCYCLIC CARBENE (NHC) LIGANDS FOR PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS

Palladium-catalyzed cross-coupling reactions have been widely studied in the past few decades, and have become powerful tools for C-C bond formation (*e.g.* Suzuki–Miyaura reaction,[12] Stille reaction,[13] Negishi reaction[14] and Heck reaction[15]) and C-N bond formation (*e.g.* Buchwald-Hartwig amination reaction[16,17]). Numerous ligands have been reported to catalyze these reactions, many of which can be functionalized with electropolymerizable groups. Incorporating a highly active palladium-based cross-coupling catalyst in to a conductive metallopolymer has the potential to create a new generation of heterogeneous catalyst. Wolf and coworkers demonstrated that a Pd-containing thiophene-based metallopolymer, synthesized by electropolymerization, was capable of catalyzing cross-coupling reactions as a heterogeneous catalyst.[18]

Among those ligands, NHC ligands are gaining more and more popularity. In 1962, Wanzlick initiated the study of NHC by synthesizing the dimerized *N,N'*-diphenylimidazol-2-ylidene.[19] Later in 1968, Ofele[20] and Wanzlick[21] synthesized the NHC based Cr and Hg complexes respectively. However, it was more than 20 years until the first thermodynamically stable and crystalline NHC, *N,N'*-diadamantylimidazol-2-ylidene (IAd), was isolated by Arduengo.[21] NHC ligands are singlet carbenes with strong σ donating properties. The occupied $p_\pi$ orbitals (perpendicular to the π-conjugated aromatic rings) of both N atoms stabilize the empty $p_\pi$ orbital of the C atom and lead to a stable singlet carbene. In IAd, this results in a significantly smaller N^C^N angle (102.2°) than that of the corresponding imidazolium salts (109.7° for tetrafluoroborate as the counterion) and elongation of N-C bond due to the loss of π-delocalization.[21] The functionality of an NHC ligand can be modified by changing the functionalities of the carbon backbones (electronic properties) and pendant groups on the N atom (steric properties). Although the

stability of an NHC varies, corresponding imidazolium or benzimidazolium salts of NHC (with a positive charge delocalized across the N^C^N moiety) are stable and can be used to generate the a free carbene *in situ* when treated with an appropriate base. Metalation of the NHC can be directly achieved using a suitable metal precursor or through transmetalation from an NHC transfer agent (*e.g.* NHC-Ag(I) complexes).




| R2 | R1 | Yield |
|---|---|---|
| F | OMe | 100% |
| | H | 100% |
| | F | 89% |
| OMe | OMe | 83% |
| | H | 72% |
| | F | 53% |

**Figure 5.** Altering the electronic density of a benzene backbone influences the reactivity of NHC ligands toward Suzuki-Miyaura reactions.[22]

Many catalytic systems using NHC ligands were developed for palladium catalyzed Suzuki-Miyaura reactions.[23] It was found that incorporating a benzene backbone allowed the tunability of the electronic properties without influencing the steric effect of the NHC ligands. Organ and coworkers synthesized a library of *ortho*-functionalized *N,N'*-diadamantyl benzimidazolium salts as the precursors for NHC ligands (Figure 5).[22] By studying the reaction between different substituted aryl chlorides and *p*-tolylboronic acids, they showed that there is a direct correlation between the increase in electronic density within the NHC backbone and the enhanced reactivity of the complex toward palladium-

catalyzed cross-coupling reactions. This was further illustrated by showing that higher electron density on the metal center leads to a faster rate-limiting oxidative addition step in the catalytic cycle.[24,25]

NHC-metal complexes can be incorporated into the thiophene-based metallopolymer (Figure 6). In 2009, Powell *et al*. reported a bithiophene functionalized NHC-Au complex and electropolymerized it into a metallopolymer (Figure 6(a)).[26] Later, conducting metallopolymers with NHC-Ag and NHC-Ir complexes were also synthesized (Figure 6(b) and 6(c)).[27] The spectroelectrochemical analysis of these metallopolymers revealed their electrochromic properties. For the Ag complex (Figure 6(b)), a stable absorption band near 700 nm appeared upon increasing the oxidative potential from 0.0 V to +1.5 V and the metallopolymer underwent a sharp color change from yellow to dark red. The Ir complex (Figure 6 (c)) showed increased absorption at 692 nm and 1092 nm upon increased oxidative potential from 0.0 V to 1.2 V.

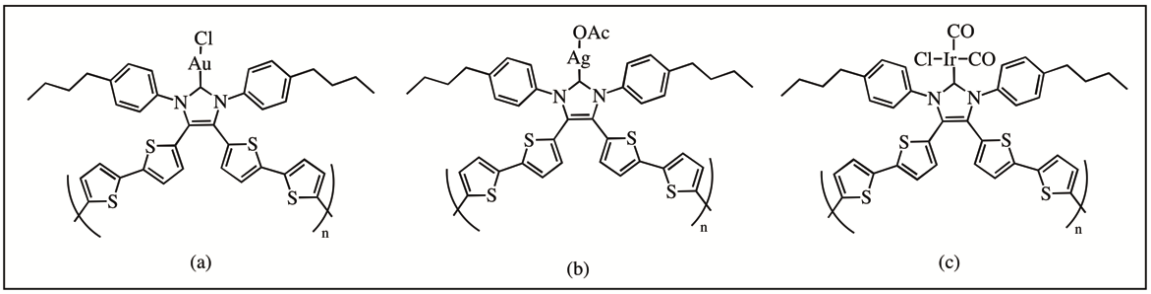



**Figure 6.** Thiophene based metallopolymer incorporating an NHC-metal complex.[26,27]

### 1. 4 DESIGN OF THE MOLECULES AND SCOPE OF THIS WORK

The thiophene-functionalized benzimidazolium salts as the precursors of the corresponding NHC were designed (Figure 7(a)). It was hypothesized that the NHC moiety

within the molecule will possess high catalytic reactivity toward the palladium-catalyzed cross-coupling reactions (*e.g.* Suzuki-Miyaura coupling) while the thiophene groups orthogonal to the N atoms will be electropolymerizable into the metallopolymer. For this metallopolymer, the electron density of the metal center can be directly tuned by applying a voltage across the π-conjugated backbone. Previous studies have shown that the β-thienyl benzene moieties are electropolymerizable and can be further functionalized by Scholl oxidation followed by bromination with *N*-bromo-succinimide.[28,29] This allows for further modification of the molecules. The pendant groups on the N atoms increase the steric hindrance around the metal center. This increases the rate of reductive elimination during the catalytic cycle and prevents potential by-products, e.g. β-hydride elimination in an alkyl-alkyl Negishi reaction.[25] The potential studies that could be done on this new type of NHC ligands are proposed in Figure 7(b). The synthesized β-thienyl-benzimidazolium salts will be metalated with a palladium precursor *via* direct metalation or transmetalation from the corresponding NHC-Ag transfer agent. The catalytic and electrochemical properties of each ligand and their corresponding Pd complexes and conducting metallopolymers will be studied. The tunability of the resulting metallopolymers as cross-coupling reaction catalysts will be investigated by measuring the kinetics of the reaction under different applied voltages.

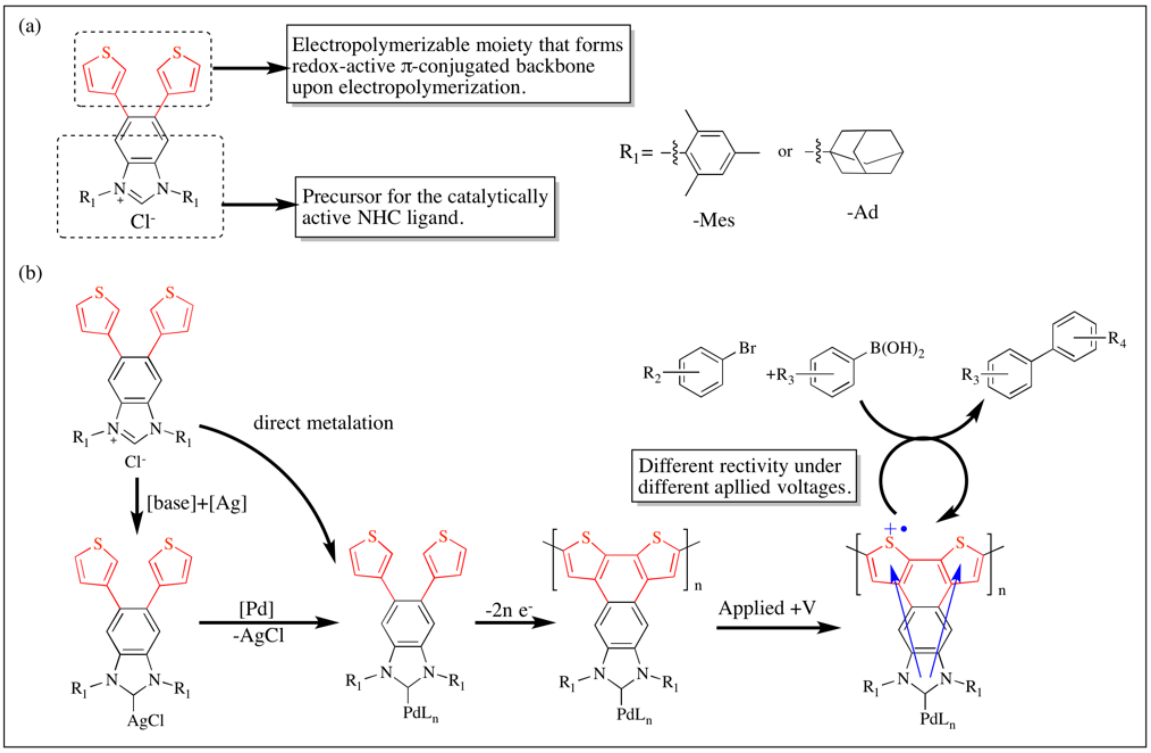



**Figure 7.** (a) Design of the NHC precursors. (b) Illustration of metalation and electropolymerization of the precursor.

Herein the synthesis of two benzimidazolium chloride precursors, 1,3-dimesityl-5,6-di(thiophen-3-yl)-*1H*-benzo[d]imidazolium chloride (DThBMesHCl) and 1,3-diadamantyl-5,6-di(thiophen-3-yl)-*1H*-benzo[d]imidazolium chloride (DThBAdHCl), will be discussed. The obstacles of the metalation and other synthetic efforts toward the final metallopolymers will be discussed in the following section. In order to compare the influence of the thiophene moieties to the benzimidazolium chloride from chemical and electrochemical perspectives, 1,3-dimesityl-*1H*-benzimidazolium chloride (BMesHCl) was synthesized by following a literature procedure.[30] Its electrochemical behavior and coordination behavior with Ag(I) were studied and compared with DThBMesHCl.

# 2. Results and Discussion

## 2. 1 SYNTHESIS OF THIOPHENE-FUNCTIONALIZED BENZIMIDAZOLIUM CHLORIDE

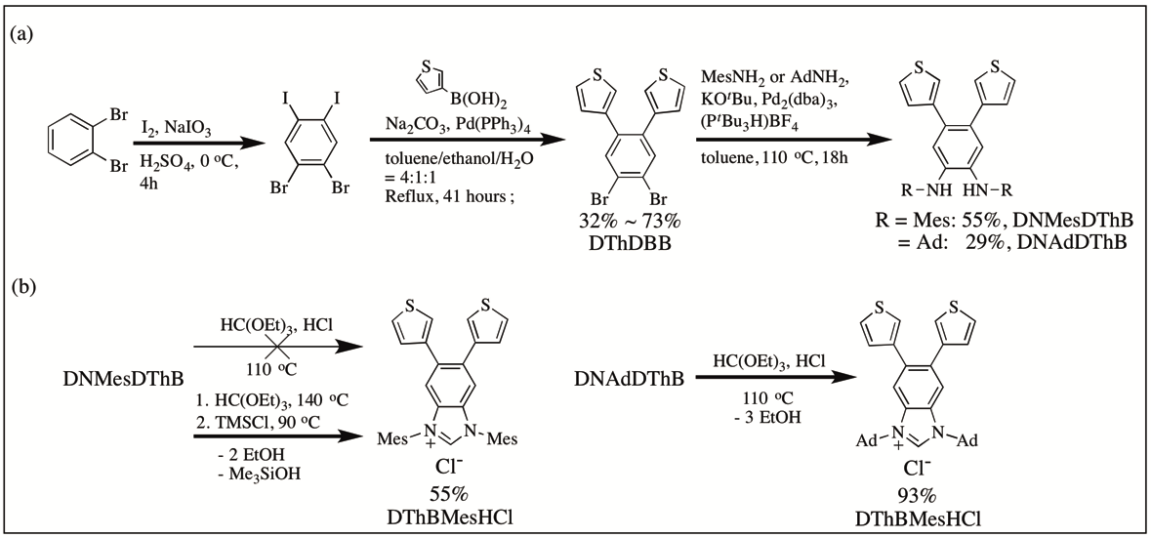


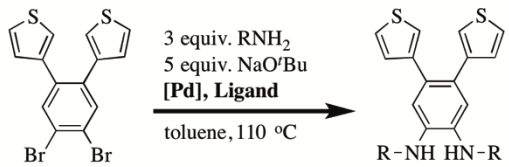

**Figure 8.** Synthetic routes toward β-thiophene-functionalized benzimidazolium salts for NHC precursors: (a) synthesis of the corresponding β-thiophene-functionalized the *o*-di-2°-amine; (b) cyclization from *o*-di-2°-amine to the corresponding benzimidazolium chloride.

The syntheses of the thiophene-functionalized benzimidazolium salts are shown in Figure 8. The routes were designed to utilize the cyclization of corresponding *o*-di-2° amines, which were synthesized from palladium-catalyzed amination (($^t$Bu$_3$PH)BF$_4$/Pd$_2$(dba)$_3$ as the ligand/palladium source) between 1,2-dibromo-4,5-diiodobenzene and corresponding primary amine (mesitylamine (MesNH$_2$) and adamantylamine (AdNH$_2$)). The synthetic routes started with the attachment of bis-β-thiophene moieties on the 1,2-dibromo-4,5-diiodobenzene by a Suzuki-Miyaura reaction. Due to the faster oxidative addition of aryl iodides than aryl bromides,[31] the reaction

between 1,2-dibromo-4,5-diiodobenzene and thiophene-3-bronic acid had high selectivity to generate 4,5-di-(3-thionyl)-1,2-dibromobenze (DThDBB), although the yield varied from 32% to 73%.

Multiple conditions were tested for the synthesis of the o-diamine from DThDBB. [1,1'-bis(diphenylphosphino)-ferrocene] palladium(II) dichloride ((dppf)$PdCl_2$)[32] and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP)[22,33] are a first-generation catalytic system, reported by Hartwig and Buchwald respectively, for the palladium catalyzed amination reactions between aryl halides and primary amines (*aka*. Buchwald-Hartwig amination reaction). 2-Dicyclohexylphosphino-2',4',6'-triisopropyl-biphenyl (XPhos)[34] and bis[2-(diphenylphosphino)phenyl] ether (DPEPhos)[35] were also used as the ligands for the palladium-catalyzed amination reaction. Recently, the Buchwald group reported 2-(dicyclohexylphosphino)-3,6-dimethoxy-2',4',6'-triisopropyl-1,1'-biphenyl (BrettPhos) as an extremely active ligand for palladium-catalyzed amination reactions.[16] All of these ligands have failed to convert DThDBB to corresponding benzyl-di-*o*-2°-amine leaving the starting material unchanged. The sole exception was *r*-BINAP/$Pd_2(dba)_3$ which yielded only the mono-aminated product. This may be explained by the deactivation of the aryl bromides by the two thienyl groups. A modified literature method using ($^t$$Bu_3PH)BF_4$/$Pd_2(dba)_3$ was the only catalytic system to catalyze the reaction for both $MesNH_2$ and $AdNH_2$.[36] The synthesis of DNMesDThB (55%) gave a higher yield than the reaction of DNAdDThB (29%) (Figure 8(a)). This observation can be explained by $MesNH_2$ is a better nucleophile than $AdNH_2$ for palladium-catalyzed amination reaction, due to the lack of β hydrogens to form undesired [Pd-H] species.[16]

**Table 1.** Tested reaction conditions for palladium-catalyzed amination of 4,5-di-(3-thienyl)-1,2-dibromobenze.




| entry | $RNH_2$ | mol% [Pd] | mol% ligand | time(h) | yield (%) |
|---|---|---|---|---|---|
| 1 | $AdNH_2$ | 10% $Pd_2(dba)_3$ | 40% Xphos | 38 | - |
| 2 | | 10% $Pd_2(dba)_3$ | 50% DPEPhos | 38 | - |
| 3[a] | | 10% $(dppf)PdCl_2$ | 60% dppf | 16 | - |
| 4[b] | | 5% $Pd_2(dba)_3$ | 10% *r*-BINAP | 16 | - |
| 5 | | 7.5% $Pd_2(dba)_3$ | 18% ($^tBu_3PH)BF_4$ | 24 | 29 |
| 6[c] | $MesNH_2$ | 5% $Pd_2(dba)_3$ | 10% *r*-BINAP | 16 | [d] |
| 7[e] | | 7% $Pd(OAc)_2$ | 12% BrettPhos | 16 | - |
| 8 | | 7.5% $Pd_2(dba)_3$ | 15% ($^tBu_3PH)BF_4$ | 18 | 55 |

a. reaction was conducted in THF at 100 °C. b. reaction was conducted at 140 °C. c. reaction was conducted at 120 °C. d. 50% mono-aminated product was isolated. e. reaction was conducted in 1,4-dioxane at 80-100 °C.

Syntheses of benzimidazolium salts from the cyclization of *o*-diamines can be achieved by reaction with $HC(OEt)_3$ in presence of a protonic acid, *e.g.* HCl or $NH_4BF_4$.[22,23] In this work, the reaction was conducted with $HC(OEt)_3$ and HCl in a distillation apparatus with a Vigreux column at 110 °C to remove the EtOH (b.p 78 °C) generated, but not $HC(OEt)_3$ (b.p 143 °C). DThBAdHCl was synthesized by following this protocol in 93% yield (Figure 8(b)). DThBMesHCl could not to be synthesized using the same protocol. Literature has shown that cyclization of the benzimidazolium salts with bulky aromatic pendant groups on both N atoms can be complex.[37,38] Grieco *et al*. reported[30] a facile

cyclized method by heating the corresponding *o*-diamine species with $HC(OEt)_3$ to form a N-C(HOEt)-N intermediate followed by addition of trimethylsilyl chloride (TMSCl) to remove one equivalent of $EtO^-$ as TMSOEt, leaving $Cl^-$ as the counterion; the DThBMesHCl was cyclized by this protocol in 55% yield.

## 2. 2 CYCLIC VOLTAMMETRY STUDY OF DTHBMESHCL AND BMESHCL

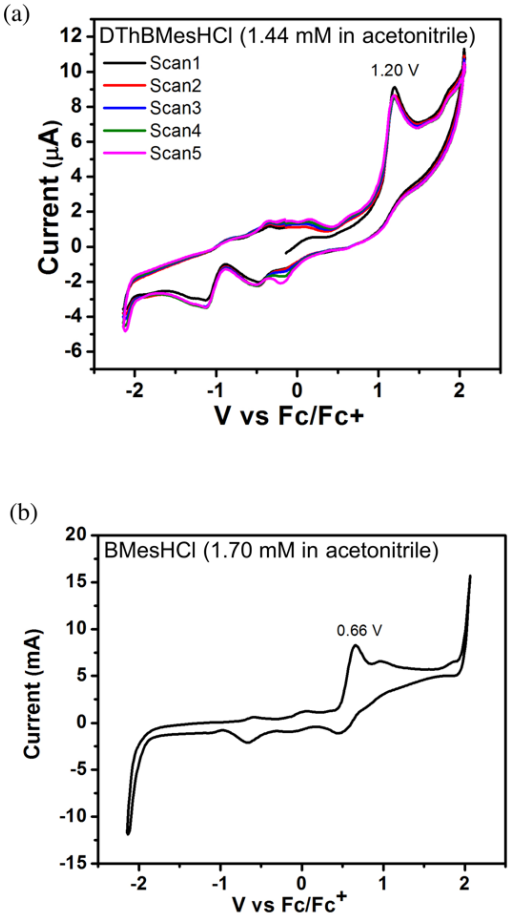



**Figure 9.** Cyclic voltammetry study of (a) DThBMesHCl ($1.6 \times 10^{-3}$ mol/L in acetonitrile); (b) BMesHCl ($1.6 \times 10^{-3}$ mol/L in acetonitrile).

Cyclic voltammetry (CV) of DThBMesHCl ($1.6 \times 10^{-3}$ mol/L in acetonitrile, see 4. Experimental Details section for more information) is shown in Figure 9(a). A successful electropolymerization will deposit the polymer/oligomer onto the electrode. This increases the overall conductivity of the electrode and leads to obvious increase of the measured current as number of scans increases. Five scans were conducted in order to explore the potential electropolymerization reaction through the β-thienyl moieties. Similar β-thienyl benzene reported by Tovar *et. al.* showed two irreversible responses at +0.83V and +0.91V,[29] which correspond to the intramolecular cyclization between two thiophenes and intermolecular oxidative polymerization. In our study, no obvious current increase was observed with increased scan number. This indicates no cyclization or polymerization occurred during electrochemical oxidation. The irreversible response at +1.20 V is assigned to the one $e^-$ oxidation of the entire polycyclic system of the molecule, forming a radical cation. No polymerization or cyclization response was seen even at potentials as positive as +2.05 V.

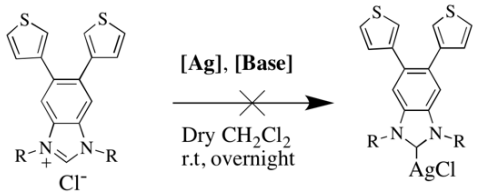
CV of BMesHCl ($1.7 \times 10^{-3}$ mol/L in acetonitrile) was studied for the comparison with DThBMesHCl and is shown in Figure 9(b). A similar trend was observed with an irreversible oxidation response at +0.66 V. Since BMesHCl does not have two β-thiophene moieties, the response at +0.66 V can only be explained as a one $e^-$ oxidation of the polycyclic rings. Compared to the DThBMesHCl, this response has a much lower potential ($\Delta V = 0.54$ V). This lowered potential indicates that the π-system is expanded by 2 additional thiophene groups and alters the electronic nature of the benzimidazolium chloride. Also, electropolymerization could be inhibited by the positive charge of the benzimidazolium which leads to more electron-deficient thiophene moieties.

## 2. 3 METALATION OF THIOPHENE-FUNCTIONALIZED NHC

Metalation of both synthesized benzimidazolium salts failed under multiple conditions.

First, direct metalation with a Pd precursor was tested. Nolan and coworkers reported a NHC-Pd(acac)Cl complex (acac: acetylacetonate) for cross-coupling reactions with a high catalytic activity and a facile synthesis.[39] This complex can be synthesized from refluxing the corresponding imidazolium chloride and $Pd(acac)_2$ in dioxane. By applying the same strategy, however, DThBAdHCl remained unchanged (100 ºC in a 2:1 mixture of dry dioxane and dry acetonitrile, dry acetonitrile was used to increase the solubility). DThBMesHCl showed no conversion in dry acetonitrile (room temperature for 22h) and generated complex products in a 4:1 mixture of dry dioxane and dry acetonitrile. These conditions proved to be inefficient methods to prepare the thiophene-functionalized NHC-Pd complexes.

**Table 2.** Tested reaction conditions for synthesis DThBMes-Ag-Cl and DThBAd-Ag-Cl.




| Entry | Benzimidazolium Chloride | [Ag] | [Base] |
|---|---|---|---|
| 1 | DThBMesHCl | 1.25 equiv. $Ag_2O$ | - |
| 2 | | 1 equiv. $AgNO_3$ | 12 equiv. $K_2CO_3$ |
| 3 | | 1 equiv. $AgNO_3$ | 2 equiv. KO$^t$Bu |
| 4 | DThBAdHCl | 0.5 $Ag_2O$ | - |
| 5 | | 1.1 equiv. $AgNO_3$ | 10 equiv. $K_2CO_3$ |
| 6 | | 3 equiv. $AgNO_3$ | 10 equiv. $K_2CO_3$ |

A well-established method for synthesis of a NHC metal complex involves the synthesis of a NHC-Ag(I)-L complex as a NHC transfer agent followed by transmetalation with the corresponding transition metal precursor to synthesize the target complex.[40,41] NHC-Ag(I) complexes have relatively good air and light stability as well as a straightforward syntheses.[41,42] Previously, transmetalation from NHC-Ag(I) complexes have been used for the synthesis of NHC-Pd(II) complexes.[40]

Table 2 summarizes the reaction conditions that failed to produce the corresponding NHC-Ag(I) complexes for both DThBMesHCl and DThBAdHCl. The simplest and most common method for the synthesis of NHC-Ag(I) complexes involves using $Ag_2O$ to react with a (benz)imidazolium chloride. The basicity of $Ag_2O$ allows for the generation of deprotonated (benz)imidazolium chloride and generation of NHC-Ag(I)-Cl simultaneously. Both DThBMesHCl and DThBAdHCl showed no conversion when reacted with $Ag_2O$ (Table 2, entry 1 and 4). NHC-Ag(I) complexes synthesized from the imidazolium chloride and $AgNO_3$ in presence of a mild base ($K_2CO_3$) with high yield (over 90%) were also reported.[43] However no conversion was observed for either benzimidazolium salts by following the same protocol (Table 2, entry 2 and 5). Furthermore, using stronger base ($KO^tBu$) failed to give conversion as well (Table 2, entry 3).

A possible factor that may inhibit metalation is the thiophene moieties forming an intermediate with metal ions through a weak coordination interaction, thereby preventing metalation with the carbene moiety. Although not common, thiophene has been reported to coordinate to metals (*e.g.* Mn, Ru and Ir) through $\eta^2$, $\eta^4$ and $\eta^5$ interactions or directly through the S atom.[44-46] In order to compensate for potential interactions between the thiophene moieties and Ag(I) ions, 3 equiv. of $AgNO_3$ was used in the presence of a large excess of $K_2CO_3$ (Table 2, entry 6); no conversion was observed using this protocol. At the

same time, Powell *et al*. reported[26,27] that bithiophene-functionalized NHC-Ag(I)-Cl and NHC-Ag(I)-OAc complexes have been synthesized by reacting corresponding imidazolium chloride with $Ag_2O$/AgOAc respectively in $CH_2Cl_2$. Coordination interactions between the Ag(I) ion and thiophene moieties (if any) should not be a key factor in preventing metalation.

These results are in accord with other observations from the literature. Bildstein *et al*. studied saturated and unsaturated *N-N'*-diferrocenyl-NHC (SIFc and IFc respectively) and corresponding complexes by synthesized corresponding imidazoli(dini)um salts (1,3-diferrocenyl-imidazolinium salts (SIFcHX) and 1,3-diferrocenyl-imidazolidinium chloride (IFcHX) respectively).[47] They found that both saturated and unsaturated imidazolium salts failed to generate thermodynamically stable, free carbene under standard conditions. Specifically, saturated imidazolidinium chloride, SIFcHX, was not metalated with various metal precursors (Pd(II), Hg(I) and Ag(I)), while unsaturated imidazolium salt, IFcHX, can be metalated with Ag(I). These results were attributed to the lack of acidity and the steric bulk of the ferrocene moieties. The same obstacles could prevent the metalation for both DThBMesHCl and DThBAdHCl, which are concluded as follows: (1) steric hindrance from two bulky *N*-substituted groups prevent the metalation, and (2) thiophene groups could reduce the electron density and thereby reduce the acidity of the imidazolium moiety.

In order to have a better understanding of the silver metalation of DThBMesHCl, silver metalation of BMesHCl was studied as a model with stoichiometric $AgNO_3$ and excess $K_2CO_3$. The black solid obtained has significant chemical shift changes in the $^1$H-NMR spectrum which indicated that the synthesis of the corresponding NHC-Ag(I)-Cl complex was achieved. This indicated steric hindrance from the two bulky mesityl groups did not inhibit silver metalation of BMes. In spite of that, in order to rule out the potential

steric hindrance for preventing metalation, thiophene-functionalized benzimidazolium salts with less bulky *N*-substituents (*e.g.* methyl groups) should be studied in future.

Another factor to influence the metalation can be lack of acidity of the benzimidazolium chloride. As weak electron-withdrawing groups, thiophene groups may reduce the electron density of $p_\pi$ orbitals on both N atoms resulting in a less-stabilized $p_\pi$ orbital of the C atom that inhibits the generation of a stable carbene. A combination of both the steric hindrance and the lack of acidity could prevent the metalation of thiophene-functionalized benzimidazolium chloride.

## 3. Conclusion

Wolf type 2 thiophene-based metallopolymers incorporating NHC-Pd complexes were designed. The syntheses of the corresponding β-thiophene-functionalized benzimidazolium chloride was achieved by first synthesizing the corresponding di-o-2°-amine by a palladium-catalyzed amination reaction, followed by cyclization with $HC(OEt)_3$ under varying conditions. After screening many conditions, $(^tBu_3PH)BF_4/Pd_2(dba)_3$ was determined to be the best catalytic system for the palladium-catalyzed amination reaction. Metalation of the DThBMesHCl and DThBAdHCl was tested by direct metalation with $Pd(acac)_2$ and by transmetalation from a NHC-Ag(I) transfer agents. None of the metalation methods succeeded in converting the starting material to the target metal complex. Analysis by comparison with the literature example and by studying the BMesHCl analogue for the silver metalation reaction reveals the potential obstacles are (1) steric hindrance from bulky *N*-substituents, and (2) the lack of acidity of the benzimidazolium moiety. Future studies should focus on developing methodologies to activate these benzimidazolium salts and synthesize corresponding molecules with less-bulky *N*-substituted moieties.

# 4. Experimental Details

## 4.1 General methods:

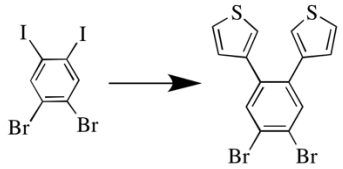
Air and moisture sensitive reactions were performed using standard Schlenk techniques under an inert atmosphere of dry nitrogen. All chemicals were purchased from commercial suppliers and were used without further purification. All of the dry solvents used, were dried using an Innovative Technology Pure Solv solvent purifier with a double purifying column. $^{1}H$ NMR (400 MHz) and $^{13}C$ {1H} NMR (100 MHz) spectra were obtained on either an Agilent MR (400 MHz) spectrometer or a Varian (400 MHz) spectrometer and were referenced to residual solvent peaks.

Electrochemical studies were performed in a glove-box under a nitrogen atmosphere using GPES software from Eco. Chemie B. V. and an Autolab Potentiostat (PGSTAT30). All electrochemical experiments were performed with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The electrolyte was purified through three recrystallizations from hot ethanol before drying under dynamic vacuum for three days at 100 $^{o}C$. All cyclic voltammetry (CV) experiments were carried out with a Pt carbon working electrode, a Pt wire coil counter electrode and a $Ag/AgNO_3$ reference electrode (silver wire dipped in a 0.01 M silver nitrate solution with 0.1 M $TBAPF_6$ in dry acetonitrile). All potentials were reported relative to the ferrocene/ferrocenium couple ($Fc/Fc^{+}$), which was used as an external standard to calibrate the reference electrode.

1,2-dibromo-4,5-diiodobenzene[48], $Pd(acac)_2$[49] and BMesHCl[30] were prepared by following literature procedures.

## 4. 2 SYNTHETIC DETAILS

### 4. 2. 1 Synthesis of DThDBB

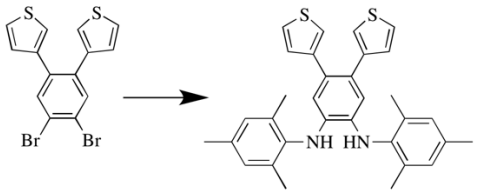



The synthesis of 1,2-bromo-4,5-di(3-thienyl)benzene was achieved with yields varying from 32% to 73%. A representative procedure is shown below.

In a sealed 250 mL 3-necked round bottom flask equipped with a condenser topped with $N_2$ in/outlet adapter, 1,2-dibromo-4,5-diiodobenzene (2.5215 g, 5.2 mmol, 1 equiv.), 3-thionylboronic acid (1.4548 g, 11.4 mmol, 2.2 equiv.) and $Na_2CO_3$ (4.3852 g, 41.4 mmol, 8 equiv.) were suspended in toluene (100 mL), ethanol (25 mL) and water (25 mL). The mixture was then de-gassed by purging with $N_2$ under vigorous stirring for 1 h. While maintaining positive $N_2$ pressure flow, $Pd(PPh_3)_4$ (596.3 mg, 0.52 mmol, 0.1 equiv.) was quickly added under a stream of $N_2$, then the flask was immediately resealed. This mixture was heated to 85 ºC to reflux for 41 h and reaction progress was monitored by TLC until the complete consumption of 1,2-dibromo-4,5-diiodobenzene. The reaction flask was then allowed to cool to room temperature and diluted with $Et_2O$ (200 mL) and transferred to a separatory funnel, where the aqueous phase was removed and the organic phase was washed by 10% HCl aqueous solution, saturated $NaHCO_3$ aqueous solution, then brine to give a clear yellow solution. The organic phase was collected and dried over $MgSO_4$ to give clear light yellow solution. After filtration, the solvent was removed by rotary evaporation and vacuum. The crude product was purified on a silica gel column with 1% (v/v) ethyl acetate in hexanes as the eluent, followed by recrystallization from hot ethanol to afford a white crystalline solid (1.30 g, 63%): $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 2H),

7.20 (dd, $J$ = 5.0, 3.0 Hz, 2H), 7.09 (dd, $J$ = 3.0, 1.3 Hz, 2H), 6.74 (dd, $J$ = 5.0, 1.3 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.75, 136.07, 134.85, 128.48, 125.52, 123.80, 123.57.

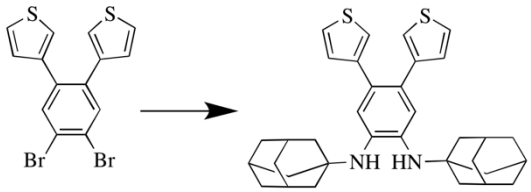
**4. 2. 2 Synthesis of DNMesDThB**




In a dry box, ($^t$Bu$_3$PH)BF$_4$ (63.9 mg, 0.22 mmol 0.15 equiv.) and Pd$_2$(dba)$_3$ (102.5 mg, 0.11 mmol, 0.075 equiv.) were dissolved by dry toluene (5 mL) in a scintillation vial. A stir bar was then added and the solution was stirred under room temperature for 30 min. Meanwhile, to a 50-mL oven-dried Schlenk flask was added DThDBB (600.1 mg, 1.5 mmol, 1 equiv.) and NaO$^t$Bu (432.9 mg, 4.5 mmol, 3 equiv.). The Schlenk flask was pumped into the dry box where the red solution of ($^t$Bu$_3$PH)BF$_4$ and Pd$_2$(dba)$_3$ in toluene was added into the Schlenk flask. Additional toluene (20 mL) was used to rinse the vial and further diluted the mixture in the Schlenk flask. The flask was then sealed with a septum and pumped out of the dry box. The mixture was further de-gassed by purging $N_2$ through the solution with vigorous stirring for 20 min, before mesitylamine (0.64 mL, 4.5 mmol, 3 equiv.) was injected in. The mixture was stirred in a pre-heated 110 ºC oil bath for 16 h. The flask was then allowed to cool to room temperature. The resulting dark solution was transferred to a separatory funnel by $Et_2O$ (100 mL) and water (50 mL). The aqueous phase was removed and the organic phase was washed by saturated $NH_4Cl$ aqueous solution, saturated $NaHCO_3$ aqueous solution, and brine before being collected and dried over $Na_2SO_4$ to give a clear dark red solution. After filtration, the solvent was removed by rotary evaporation and vacuum. The crude product was purified on a silica gel

column with 3:2 (v/v) hexanes to $CH_2Cl_2$ as the eluent and then recrystallized from a hot mixture of ethanol (50 mL) and toluene (5 mL) to afford title compound as yellow solid (421.4 mg, 55%): $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.05 (dd, *J* = 5.0, 3.0 Hz, 2H), 6.95 (s, 4H), 6.81 (dd, *J* = 3.0, 1.3 Hz, 2H), 6.63 (dd, *J* = 4.9, 1.3 Hz, 2H), 6.36 (s, 2H), 5.17 (s, 2H), 2.31 (s, 6H), 2.25 (s, 12H), 2.25 (s, 2H).

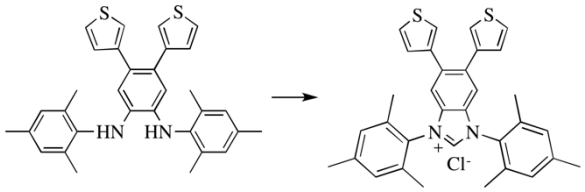
### 4. 2. 3 Synthesis of DNAdDThB




In a dry box, ($^t$Bu$_3$PH)BF$_4$ (51.7 mg, 0.18 mmol 0.18 equiv.) and Pd$_2$(dba)$_3$ (70.1 mg, 0.076 mmol, 0.075 equiv.) were dissolved by dry toluene (3 mL) in a scintillation vial with a stir bar. The solution was then stirred at room temperature for 30 min. Meanwhile, to a 25-mL oven-dried Schlenk flask was added DThDBB (402.5 mg, 1 mmol, 1 equiv.), KO$^t$Bu (451.4 mg, 4 mmol, 4 equiv.) and 1-adamantylamine (605.1 mg, 4 mmol, 4 equiv.). This Schlenk flask was then pumped into the glove box where the red solution of ($^t$Bu$_3$PH)BF$_4$ and Pd$_2$(dba)$_3$ in toluene was added into a Schlenk flask. Additional dry toluene (10 mL) was used to rinse the vial and further diluted the mixture in the Schlenk flask. The flask was then sealed with a septum and pumped out of the glove-box. The mixture was further de-gassed by purging $N_2$ through the solution under vigorous stirring for 30 min. The mixture was stirred in a pre-heated 110 °C oil bath for overnight. The flask was then allowed to cool to room temperature. The mixture was filter by a pad of silica gel topped with a layer of celite. The pad was further eluted by additional $Et_2O$ (150 mL). All the eluted liquid was combined and washed by saturated $NH_4Cl$ aqueous solution and brine in a separatory funnel before collected and dried over $Na_2SO_4$ to give a clear solution. After

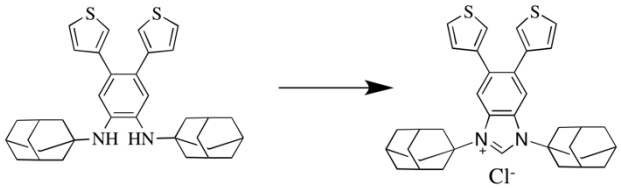
filtration, the solvent was removed by rotary evaporation and vacuum. The crude product was purified on a silica gel column with 3:2 (v/v) hexanes to $CH_2Cl_2$ as the eluent to afford title compound as a yellow solid (157.8 mg, 29%): $^1$H NMR (400 MHz, Chloroform-d) δ 7.14 (dd, *J* = 4.9, 3.0 Hz, 2H), 7.01 – 6.94 (m, 4H), 6.78 (dd, J = 5.0, 1.3 Hz, 2H), 3.69 (s, 2H), 2.13 – 2.07 (m, 6H), 1.89 (d, *J* = 2.9 Hz, 12H), 1.67 (d, *J* = 3.2 Hz, 12H).

**4. 2. 4 Synthesis of DThBMesHCl**



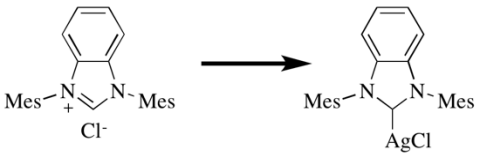

Following a modified literature procedure.[30] DNMesDThB (190.1 mg, 0.37 mmol, 1 equiv.) was dissolved by $HC(OEt)_3$ (10 mL, 60 mmol) in a 3-necked round bottom flask. The flask was then equipped with a distillation apparatus with a Vigreux column and two other necks were sealed with septa. The mixture was then heated to 155 °C for 2 h. The oil bath was then allowed to cool to 95 °C and trimethylsilyl chloride (TMSCl) (neat, 2 mL) was injected in. This mixture was then reflux under 95 °C and approximately 1 mL liquid (a mixture of TMSCl and EtOH) was distilled. Another portion of TMSCl (neat, 0.5 mL) was injected in and the mixture was then allowed to reflux for another 10 min. The mixture was then allowed to cool to room temperature. The resulting dark solution was filtered under reduced pressure to collect the title compound as a black powder (53.2 mg, 26%): $^1$H NMR (400 MHz, Acetonitrile-$d_3$) δ 9.27 (s, 1H), 7.51 (s, 2H), 7.34 – 7.25 (m, 8H), 6.77 (d, *J* = 4.6 Hz, 2H), 2.45 (s, 6H), 2.14 (s, 12H).

**4. 2. 5 Synthesis of DThBAdHCl**



Following a modified literature procedure.[22] DNAdDThB (108.7 mg, 0.2 mmol, 1 equiv. ) and HCl (12.1 N aqueous solution, 0.1 mL, 1.21 mmol, 6 equiv.) were dissolved by $HC(OEt)_3$ (10 mL, 60 mmol). The mixture was allowed to stir at room temperature for 30 min before heating at 80 ºC overnight (16 h). The mixture was then allowed to cool down to room temperature, and transferred to separatory funnel by $Et_2O$ (50 mL) and toluene (10 mL). The mixture was washed by a saturated $NaHCO_3$ aqueous solution and brine then collected and dried over $Na_2SO_4$ to give a clear solution. After filtration, the solvent was removed by Schlenk line to afford the title compound as a yellow solid (109.2 mg, 93%): $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.97 (s, 2H), 7.24 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.13 (dd, *J* = 3.0, 1.3 Hz, 2H), 6.76 (dd, *J* = 5.0, 1.3 Hz, 2H), 2.64 (d, *J* = 2.1 Hz, 12H), 2.36 (s, 6H), 1.85 (dd, *J* = 25.7, 13.0 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.58, 139.26, 134.19, 130.81, 128.78, 125.86, 124.21, 117.48, 63.20, 41.26, 35.74, 29.76.

**4. 2. 5 Synthesis of BMesAgCl**

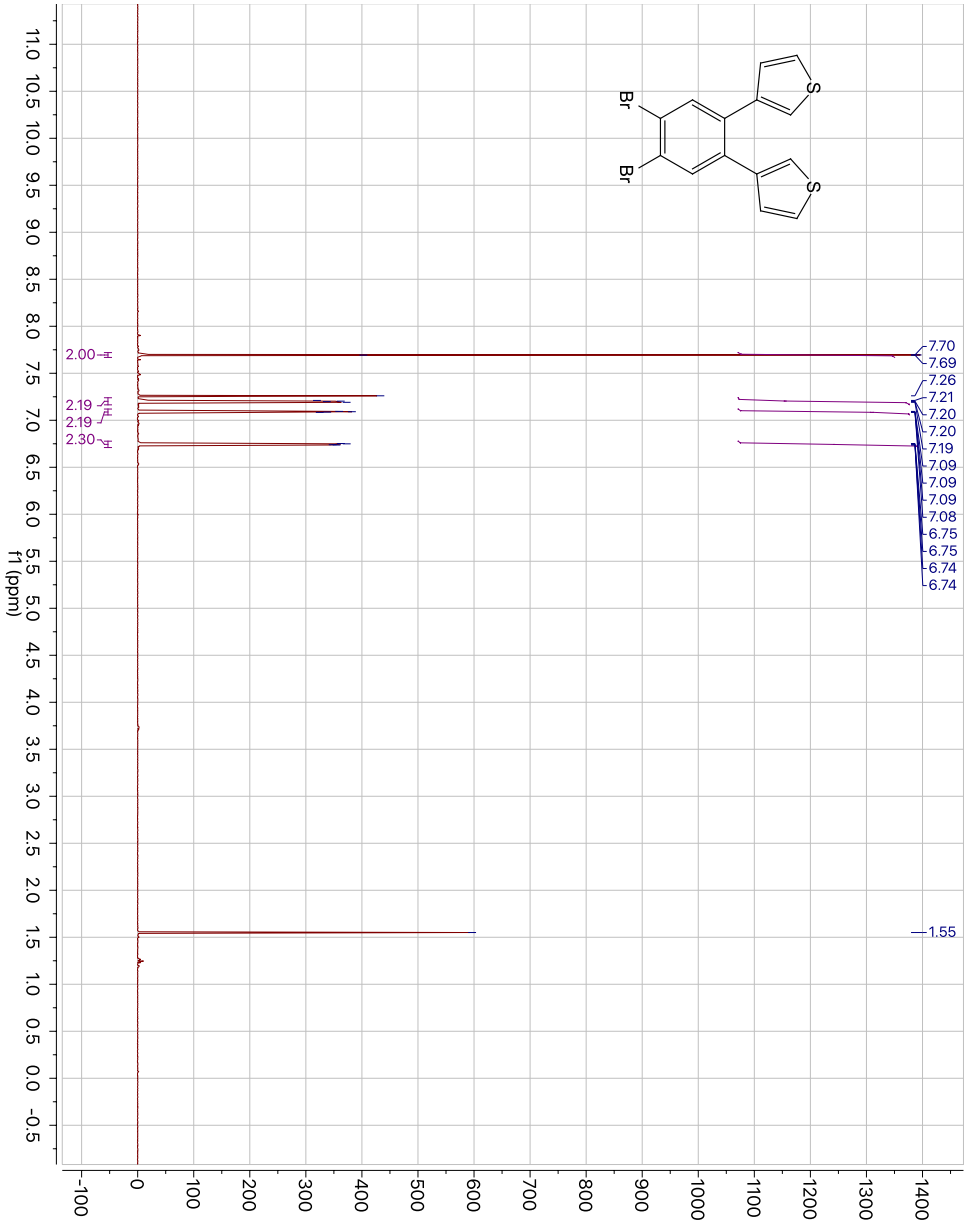


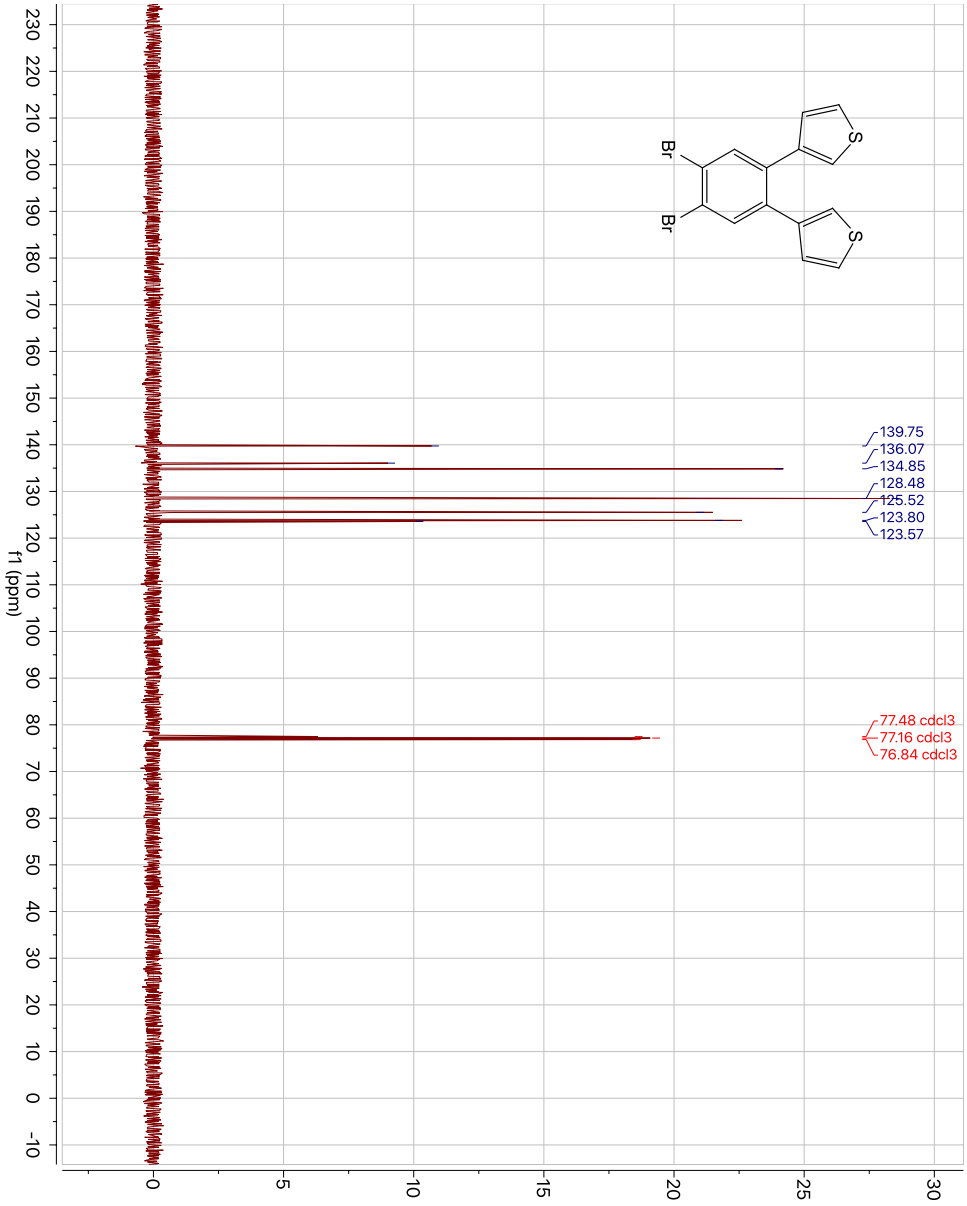
BMesHCl (41 mg, 0.105 mmol, 1 equiv.) and $AgNO_3$ (18.6 mg, 0.109 mmol, 1 equiv.) were suspended in $CH_2Cl_2$ (10 mL) and stirred at room temperature for 5 min before $K_2CO_3$ (144 mg, 10.43 mmol, 10 equiv.) was added to the stirring solution in one portion. The solution was then stirred at room temperature for another 2 h before the mixture was

filtered. The solution was then condensed by rotary evaporation to approximately 1 mL in volume. The resulting dark mixture was precipitated by addition of $Et_2O$ (10 mL). The solid was collected by filtration under reduced pressure and dried under vacuum to afford the title compound as a dark solid (10.8 mg, 20%): $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 6.2, 3.1 Hz, 1H), 7.06 (dd, *J* = 6.1, 3.1 Hz, 1H), 7.03 – 7.00 (m, 2H), 2.50 (s, 3H), 1.68 (s, 6H).

# Appendix

NMR spectra for compounds of interest.


Br
Br
S
S
2.00
2.19
2.19
2.30
7.70
7.69
7.26
7.21
7.20
7.20
7.19
7.09
7.09
7.09
7.08
6.75
6.75
6.74
6.74
1.55
f1 (ppm)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Br
S
S
139.75
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123.80
123.57
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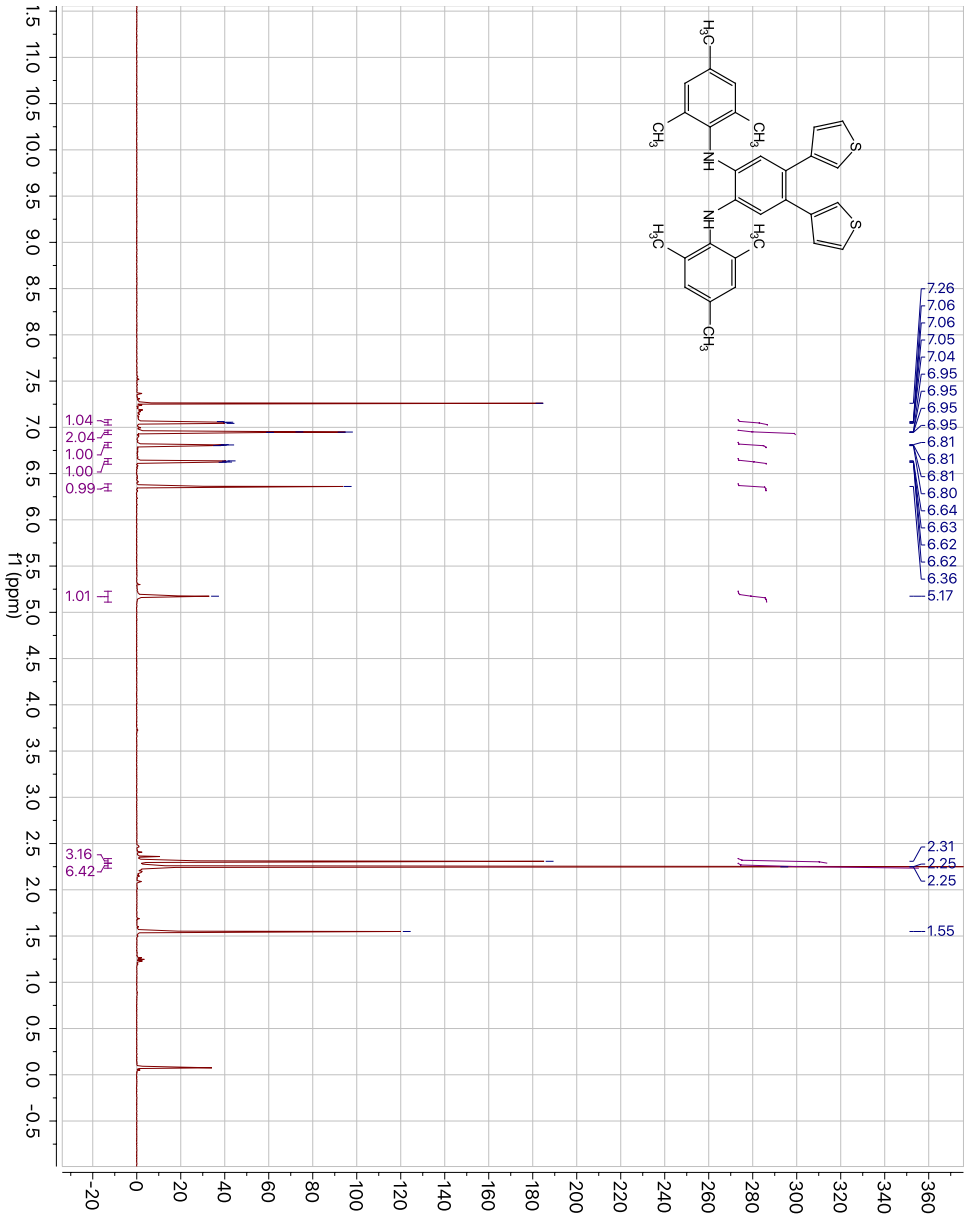
76.84 cdcl3
f1 (ppm)


f1 (ppm)
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1.00
0.99
1.01
3.16
6.42
7.26
7.06
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7.04
6.95
6.95
6.95
6.95
6.81
6.81
6.81
6.80
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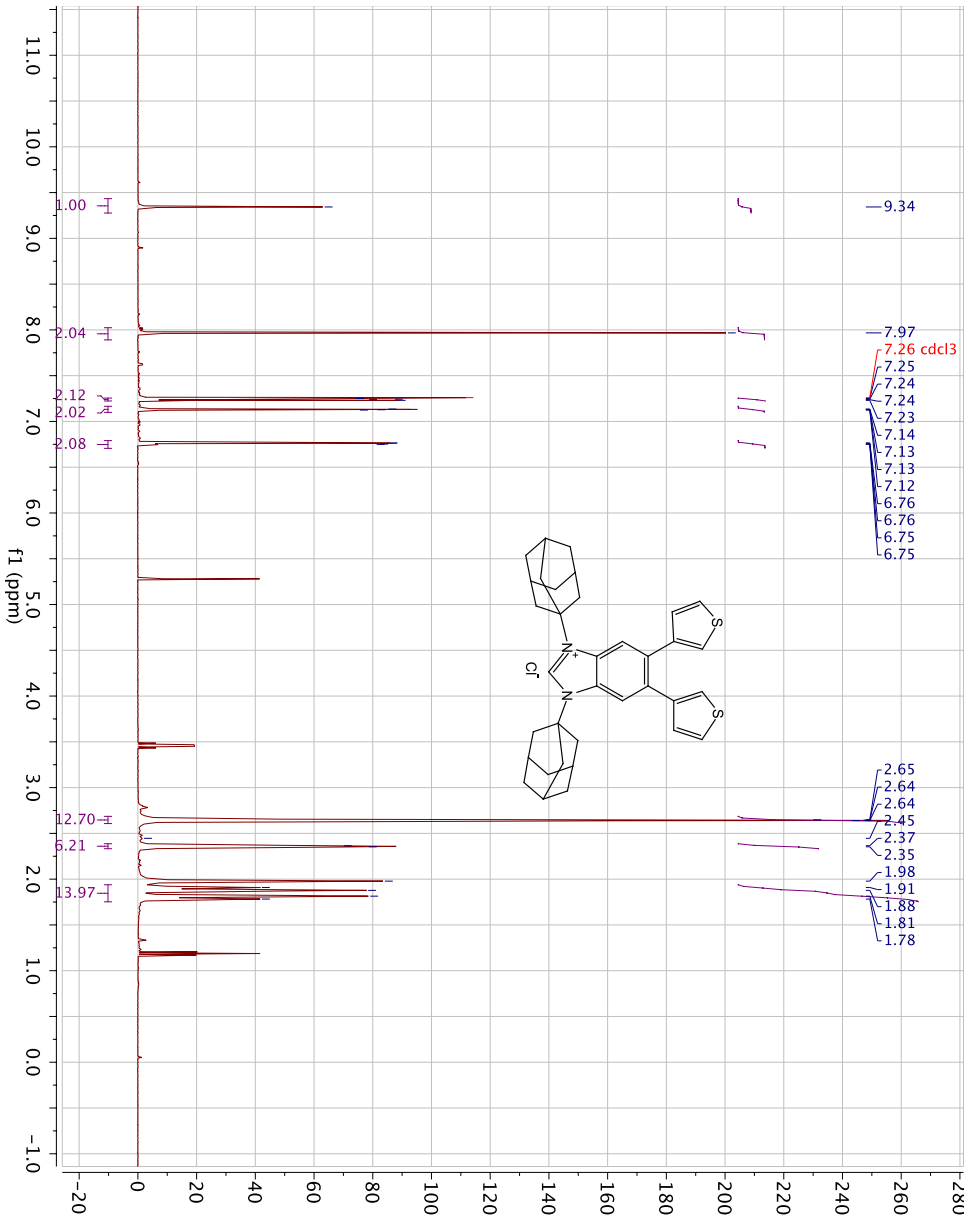
H3C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2.02
2.08
12.70
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13.97
9.34
7.97
7.26 cdcl3
7.25
7.24
7.24
7.23
7.14
7.13
7.13
7.12
6.76
6.76
6.75
6.75
2.65
2.64
2.64
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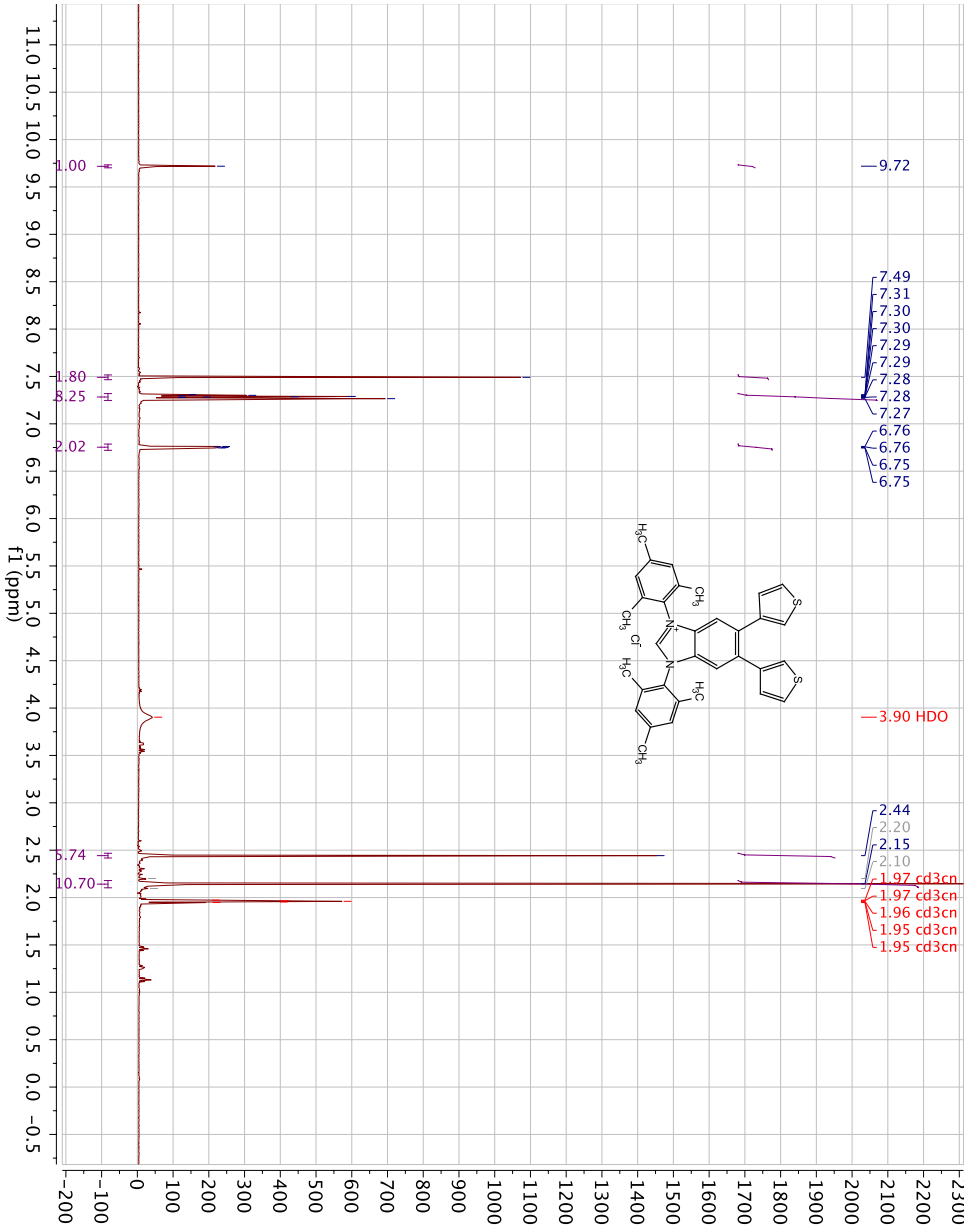
N+
N
S
S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2.02
5.74
10.70
9.72
7.49
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
6.76
6.76
6.75
6.75
3.90 HDO
2.44
2.20
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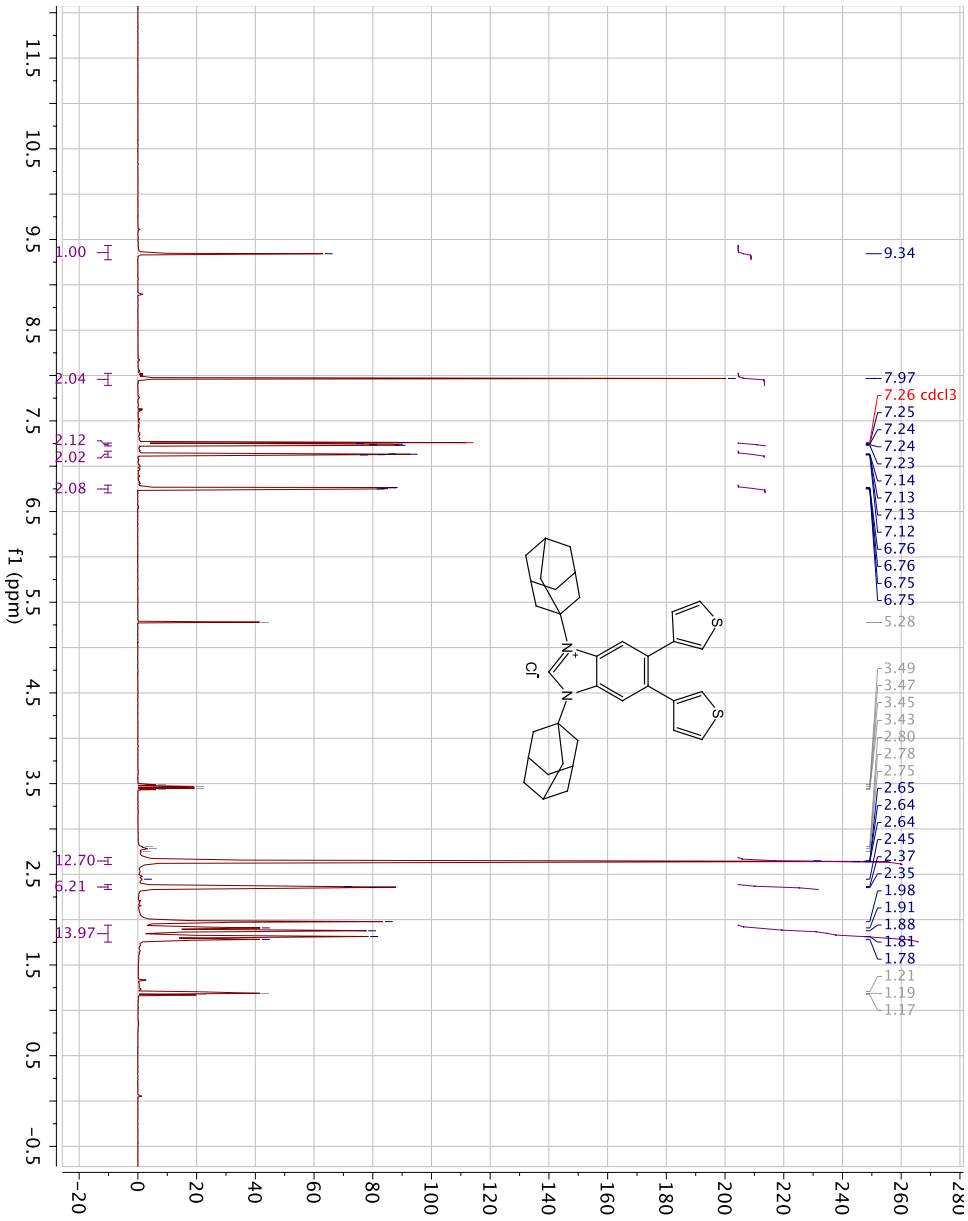
f1 (ppm)


f1 (ppm)
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2.12
2.02
2.08
12.70
6.21
13.97
9.34
7.97
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7.24
7.24
7.23
7.14
7.13
7.13
7.12
6.76
6.76
6.75
6.75
5.28
3.49
3.47
3.45
3.43
2.80
2.78
2.75
2.65
2.64
2.64
2.45
2.37
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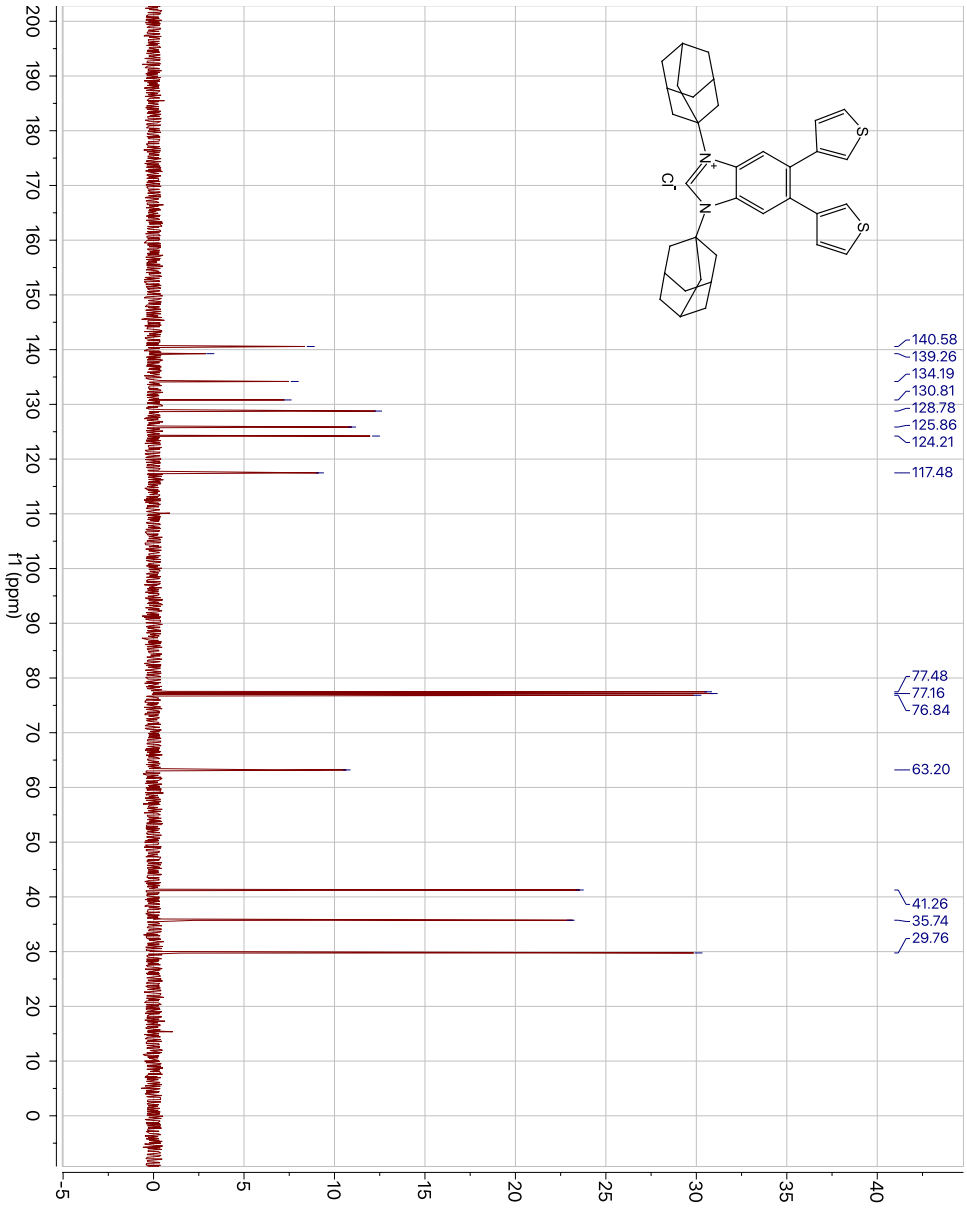
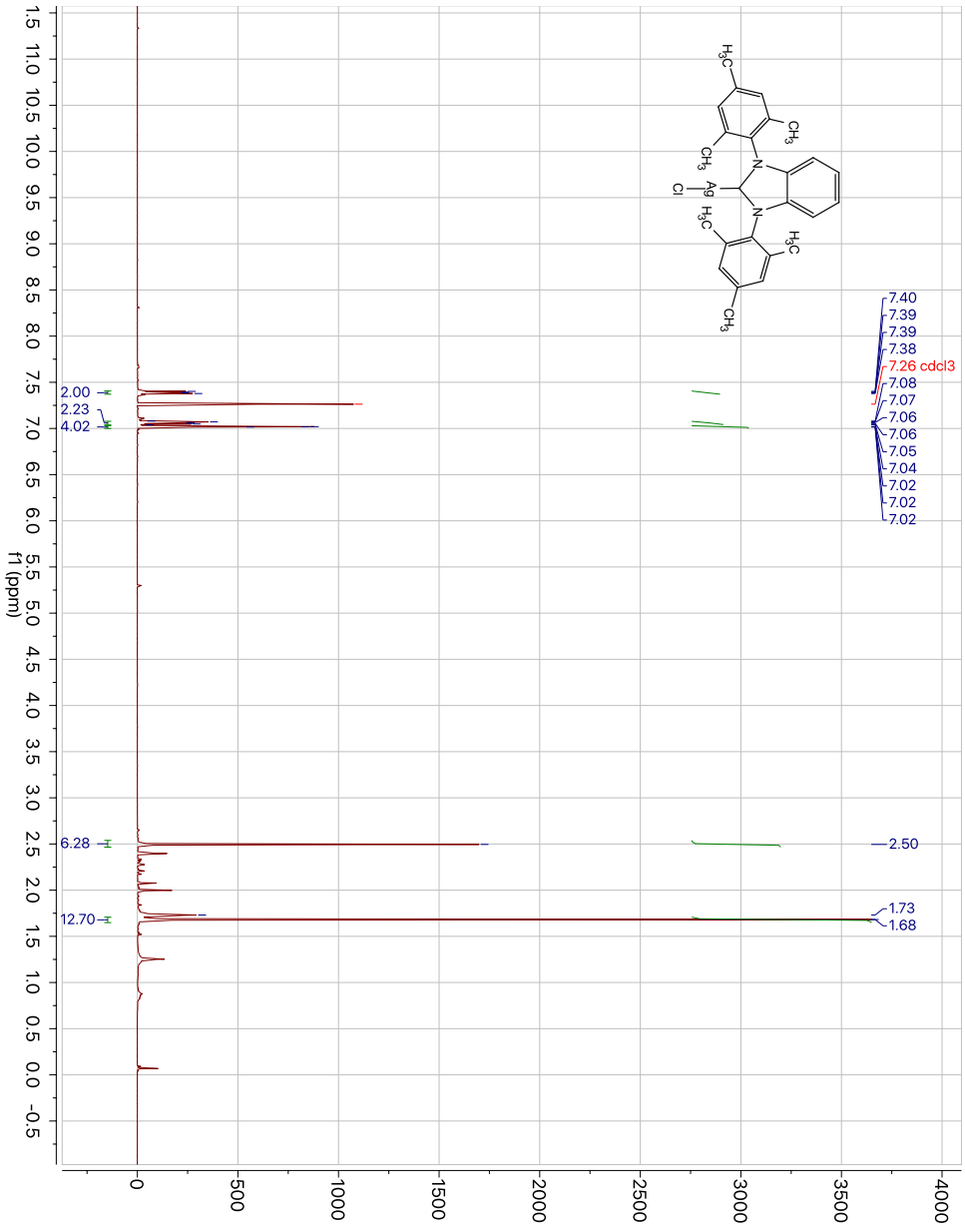
N+
N
S
S


f1 (ppm)
140.58
139.26
134.19
130.81
128.78
125.86
124.21
117.48
77.48
77.16
76.84
63.20
41.26
35.74
29.76
Cl-
N+
N
S
S


f1 (ppm)
2.00
2.23
4.02
6.28
12.70
7.40
7.39
7.39
7.38
7.26 cdcl3
7.08
7.07
7.06
7.06
7.05
7.04
7.02
7.02
7.02
2.50
1.73
1.68

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